Behavior of Optical Phonons near the Diffuse Phase Transition in Relaxor Ferroelectric PbMg$_{1/3}$Ta$_{2/3}$O$_3$

S.G. Lushnikov*

Ioffe Physical Technical Institute, 26 Politekhnicheskaya, 194021, St. Petersburg, Russia

S.N. Gvasaliya†

Laboratory for Neutron Scattering ETHZ & Paul-Scherrer Institut CH-5232 Villigen PSI Switzerland

R.S. Katiyar

University of Puerto Rico, P.O. Box 23343, San Juan, USA
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Raman scattering in relaxor ferroelectric PbMg$_{1/3}$Ta$_{2/3}$O$_3$ (PMT) was investigated in the single crystalline form in the temperature range of 20 - 295 K. Anomalous temperature dependence of the integrated intensity and the Raman line contours were found at the diffuse phase transition. A correlation between the anomalies in the integrated intensities and the dispersion of the dielectric response was observed. The distortions of Raman lines with decreasing temperature are discussed.

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The ferroelectric state in partially disordered crystals has attracted considerable attention of researchers due to their anomalously high dielectric constant over a broad temperature range near the phase transitions. The most suitable model objects for the studies of the ferroelectric state in partially disordered crystals are complex perovskites with the common formula AB$'_x$B$''_{1-x}$O$_3$ [1]. In some compounds of this family, the transition into a ferroelectric phase drastically differs from the classical ferroelectric phase transitions observed in perovskites and manifests itself as wide (several hundred degrees) frequency-dependent anomalies of physical properties referred to as a diffuse phase transition [1]. This group of compounds is called relaxor ferroelectrics, or simply relaxors [2]. At first it was believed that such an anomalous lattice dynamics is due to composition fluctuations accompanied with or without local phase transitions [1]. Later it was found that the relaxor ferroelectrics are homogeneous, but have nanoregions with 1:1 ordering of B$'$ and B$''$ ions [3] that play an important role in lattice dynamics of complex perovskites.

In relaxors, the transformation into a ferroelectric phase can be accompanied by a first-order structural phase transition. In some cases the structural instability of a crystal is pronounced in lattice dynamics, as, for instance, in relaxor ferroelectric PbSc$_{1/2}$Ta$_{1/2}$O$_3$ [1]. In other cases, it can be suppressed, and then it is realized only under an applied external electric field as, for instance, in PbMg$_{1/3}$Nb$_{2/3}$O$_3$ (PMN) [1]. Probably, this feature does not exert a considerable influence on lattice dynamics in the paraelectric phase, but it should be taken into consideration in studies of the nature of the ferroelectric relaxor state. The most suitable object for studies of the transformation into the relaxor state is PbMg$_{1/3}$Ta$_{2/3}$O$_3$ (PMT) - an analog of PMN [1]. The lattice dynamics of the PMT crystal has been investi-

gated by dielectric [4] and optical [5, 6] spectroscopy, neutron scattering [7, 8], and adiabatic calorimetry [9] in a wide temperature range, but, to our knowledge, no anomalies except the relaxor one have been revealed even under an applied electric field. The transformation into the ferroelectric phase in PMT is accompanied by a broad frequency-dependent anomaly of the dielectric response with a maximum at a frequency of 10 kHz in the vicinity of 170 K, which is well described by the Vogel-Fulcher law [4]. In the entire range of temperatures and applied electric fields, the macroscopic symmetry of PMT does not vary and remains cubic Pm$\bar{3}$m [1, 10].

In experimental studies of lattice dynamics of PMT, polarized first-order Raman scattering was observed [5, 6], which contradicts X-ray structural investigations [1, 10] because first-order Raman scattering is forbidden by the selection rules for cubic crystals with the perovskite structure. It is important to note that first-order Raman scattering was observed for nearly all complex perovskites [11]. The nature of this scattering is a subject of discussion; the only commonly accepted point of view is that Raman scattering and the short-range order in distribution of B$'$ and B$''$ ions (in our case, Mg and Ta) are related. Different ideas on the nature of Raman scattering in complex perovskites were analyzed in detail in [11, 12], and we shall not dwell on them here. Note only that Raman spectra of a major part of complex perovskites are similar to each other.

Raman scattering studies of lattice dynamics of complex perovskites were performed in detail in the paralectric phase [12]. The evolution of low-frequency Raman spectra of PMN, a model object for studies of relaxor ferroelectrics, was investigated in an unsuccessful search for soft modes in a wide temperature range [11, 12, 13, 14]. There is considerably less information on the behavior of optical phonons in the vicinity of the diffuse phase tran-

sition. In the work reported here we carried out Raman scattering investigations of the PMT crystal to obtain data on the behavior of optical phonons in the case of a purely 'relaxor behavior' of the lattice dynamics.

Raman spectra were excited with an argon laser and analyzed with a triple grating spectrometer ISA Model T64000 equipped with a liquid nitrogen cooled CCD detector. The backscattering spectra were recorded using a Raman microprobe system. The illumination of the sample was adjusted before measurements at each temperature to optimize the signal. Measurements were performed using a modified Cryogenic Tech. Closed-cycle Refrigerator Model 20 with a Lake Shore DRS-84C temperature controller. The diagonal $X(YY)\bar{X}$ and off-diagonal $X(YZ)\bar{X}$ spectra were collected with X, Y and Z-axes being along the four fold directions of the PMT cubic lattice. When discussing spectra and assigning the lines, we adopted the notations used in [6]. Raman measurements were carried our on a high-quality single-crystal of PMT $6.5 \times 4.5 \times 1.6$ mm^3 in size. The same single crystal was used for neutron scattering [7] and Brillouin light scattering [4] experiments. No changes in the crystal quality were observed upon thermal cycling.
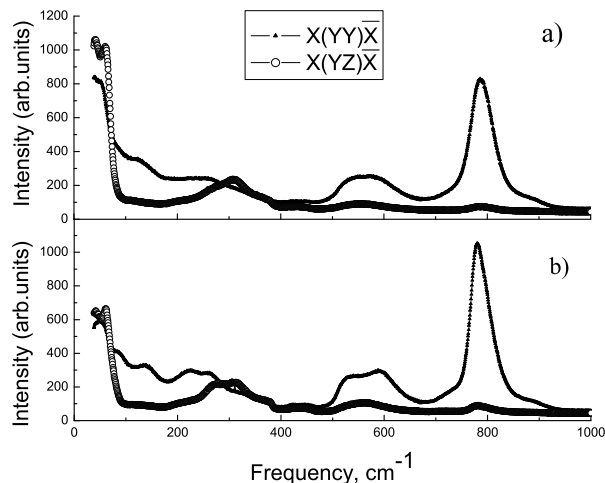

FIG. 1: The diagonal and off-diagonal Raman spectra of PMT T=285 K (a) and T=134 K (b). Note the shape deformation of high frequency A1g mode at lower temperature.

Figure 1 shows Raman spectra of the PMT crystal for both diagonal and off-diagonal polarizations at two temperatures. The off-diagonal $X(YZ)\bar{X}$ spectra consist of two modes with characteristic frequencies 80 cm^{-1} and 300 cm^{-1}. Due to similarity with the spectrum of complex perovskites [6, 11], it was concluded that these modes are of the T_{2g} symmetry and are related to the Pb and O motion. The diagonal $X(YY)\bar{X}$ spectra are richer - they consist of four modes with 80, 240, 580, and 800 cm^{-1}. As pointed out in [6, 11], the intense line in

the diagonal spectra at 800 cm^{-1} is the A_{1g} mode. It represents the breathing-type motion of oxygen ions in the octahedral. There are two significant changes in the PMT spectra as the temperature decreases below room temperature: a strong decrease of the intensity below 200 cm^{-1} and the A_{1g} mode asymmetry.

Experimental results were analyzed by using calculations of integrated reduced Raman scattering intensity given by:

$$S = \int_{\omega_1}^{\omega_2} \frac{I}{n(\omega) + 1} d\omega, \qquad (1)$$

where ω_1 and ω_2 are the boundaries of Raman bands and $n(\omega)$ is the Bose population factor. The integrated intensity is proportional to susceptibility of a relevant mode. This approach is more correct for analysis of the temperature behavior of Raman spectra of the crystals whose line shapes are considerably distorted and damping is high. Such an analysis was successfully used for treatment of Raman measurements in a disordered perovskite $KTa_{1-x}Nb_xO_3$ [15]. It is not difficult to calculate the integrated intensity for the high-frequency A_{1g} mode in the PMT crystal, because it is well isolated in frequency from other vibrations and the integration interval is easily determined (Fig. 1). The situation with finding integration intervals for the low-frequency T_{2g} mode is much more complicated, in particular because of its proximity to the exciting line. Therefore, the choice of integration limits for calculations of the integrated intensity of the T_{2g} mode is, to a certain extent, arbitrary. The calculations performed for different integration limits have shown that qualitatively the results are the same. Only quantitative changes in the obtained anomaly (of the order of 3%) can occur. Figure 2 shows the temperature dependence of integrated reduced Raman scattering intensity of A_{1g} and T_{2g} modes. It can be seen from Fig. 2 that the integrated intensity of both A_{1g} and T_{2g} lines below 80 K and above 220 K is nearly temperature-independent, which corresponds to the predicted behavior of the first-order Raman spectrum of the crystal with temperature. The temperature dependence from 90 to 220 K is much more complicated: a decrease in temperature from room temperature at first leads to a reduction in intensity, which is pronounced for both modes, and then a sharp rise followed by a smooth fall to the temperature-independent portion of the dependence occurs. Note that the rise in the integrated intensity ΔS for the high-frequency A_{1g} mode is approximately 25% of its initial value (see Fig. 2a). This demonstrates once more how nontrivial the behavior of the vibrational spectrum of a relaxor ferroelectric is. It can hardly be expected that the high-frequency mode in the ferroelectric crystal can experience such large changes in the vicinity of the dielectric anomaly, especially in the absence of a structural phase transition.

It is interesting to compare the behavior of the Raman spectra of PMT and $BaMg_{1/3}Ta_{2/3}O_3$ (BMT), i.e.,
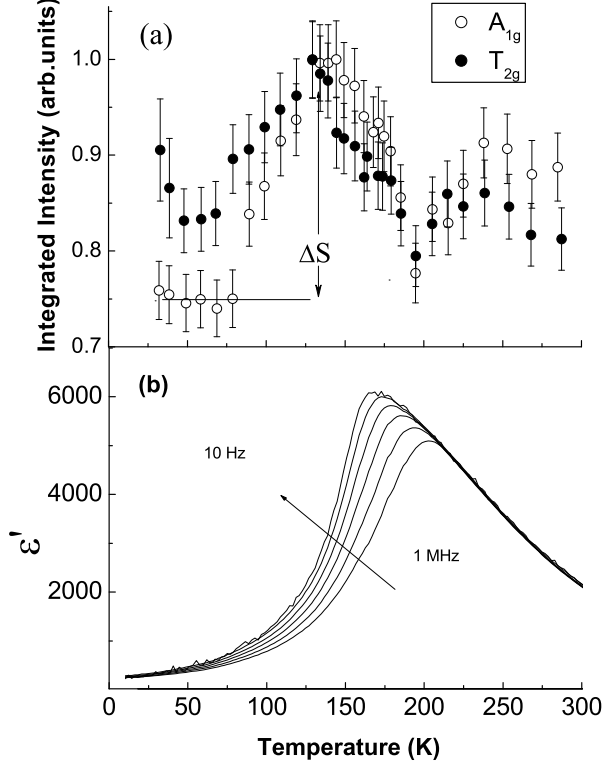
FIG. 2: Fig.2a Temperature dependences of the reduced integrated Raman scattering intensity of T_{2g} and A_{1g} modes. Fig.2b The real part of the dielectric constant of PMT (data taken from [4]).

the compound with a low dielectric constant $\varepsilon' \sim 20$ [4] where there is no phase transformation into the ferroelectric state. As noted above, the Raman spectra of PMT and BMT crystals are very similar (with the exception of the line widths), but their behavior with temperature differs considerably. As the temperature decreases (from the paraphase ~ 1100 K), the first-order Raman scattering spectra of BMT and PMT arise in the vicinity of 900 K. With further decrease in the temperature, the behavior of the Raman spectrum of BMT depends upon the temperature only slightly (the population factor is taken into account). The temperature dependences of the integrated intensities of the A_{1g} mode and other modes in BMT Raman spectra have no other anomalies except the high-temperature one [16], while Raman spectra of PMT crystals exhibit an anomalous behavior in the vicinity of the diffuse phase transition.

In the case of normal ferroelectric perovskites much attention has been paid to the soft mode dynamics. In the absence of a soft mode, anomalies in the temperature dependences of the integrated intensity of hard modes in Raman spectra in the vicinity of the phase transitions can be expected [17, 18]. These will be due to different types

of interaction between fluctuations of dielectric permeability and order parameter [18]. However, the formalism suggested in [18] is not suitable for discussing anomalies in the behavior of Raman spectra of PMT crystals where there is no structural phase transition.
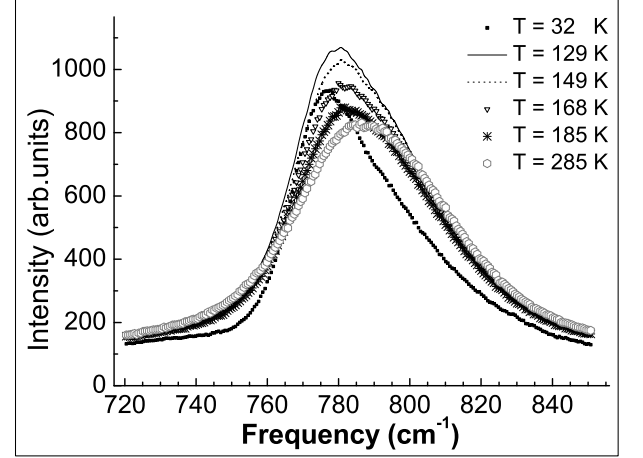

FIG. 3: Temperature evolution of A_{1g} mode of PMT crystal in the vicinity of broad dielectric anomaly.

Let us consider in detail the anomalous behavior of Raman spectra of PMT in the vicinity of transformation into the ferroelectric state by comparing them with the behavior of the dielectric response (we compare Fig. 2a and 2b). It may be concluded that i) the susceptibility of hard modes of the PMT crystal does not depend upon the temperature when there is no dispersion of dielectric permeability (it is implied that the dispersion region is somewhat wider than that shown in Fig. 2b), ii) the anomaly in the integrated intensities of Raman modes is observed just in the region of dispersion. The commonly accepted mechanism responsible for the behavior of the real part of dielectric constant in relaxor ferroelectrics is a wide spectrum of relaxation times which is frozen in the PMT crystal at $T_f = 124$ K. This temperature was determined in [4] with the help of the Vogel-Fulcher law. In Fig. 2a, the maxima in the integrated intensities of both A_{1g} and T_{2g} modes are reached at $T \sim 124$ K. It is not likely that this coincidence in temperatures is accidental. Probably, the relaxation processes giving rise to the dispersion of dielectric response are responsible for the anomalous behavior of hard modes in the Raman spectra of PMT as well. While the existence of connection between relaxation processes and the low-frequency T_{2g} mode is predictable, the connection between the high-frequency (~ 790 cm^{-1}) A_{1g} mode and the relaxation processes is absolutely unexpected. Note that a considerable change in the intensity of diffuse neutron scattering in the PMT crystal was also observed in the temperature

range of 80 - 220 K [7].

Special attention should be paid to the shape of the high-frequency A_{1g} mode that shows a nontrivial temperature evolution. It is evident from Fig. 3 that a decrease in temperature from room temperature results in distortion of the line shape. A wide but rather symmetric line shape in the paraelectric phase of the PMT crystal is distorted with decreasing temperature, becoming more symmetric and its high-frequency edge is extended on approaching 32 K. A nontrivial temperature evolution of the contour of the A_{1g} mode in relaxors was observed for the first time for the $PbSc_{1/2}Ta_{1/2}O_3$ (PST) crystal in [16]. However, evolution of the A_{1g} mode contour in the paralectric phase in PST was accompanied by its splitting and formation of an additional structure with increasing temperature. This behavior of the A_{1g} mode was attributed to the transition into an intermediate (probably, incommensurate) phase in the PST crystals and dynamic breaking of the selection rules. Due to this, the A_{1g} mode can be observed from other points of the Brillouin zone in light scattering experiments. Taking into account the X-ray and neutron diffraction data for PST, this interpretation is correct. For PMT crystals, the analysis of the X-ray and neutron diffraction data [10] did not reveal the existence of additional phases. Note also that in PMT crystals the distortion of line contours is not accompanied by the formation of an additional structure. Therefore, it is reasonable to suppose that there is a connection between the distortion of the A_{1g} line and an increase in the anharmonicity of the PMT crystal at low temperatures. This anharmonicity might be related to the formation of short-range order in PMT at low temperature. Indeed, the evolution of the neutron diffuse scattering in PMT crystal was observed at similar temperatures [7]. Attempts to describe Raman light scattering spectra by decomposing the spectra into the sum of several damped oscillators or Lorentz (Voigt) functions are not physically justified. In the absence of structural phase transitions, in order to describe the line contour it is necessary to introduce a larger number of peaks at low temperatures than at high ones, and their number is unlimited.

In summary, a detailed study of Raman scattering spectra of relaxor ferroelectric PMT crystal in the vicinity of the ferroelectric transition temperature has revealed the following:

* There is correlation in the behavior of the optic hard mode and the dielectric response in the vicinity of the diffuse ferroelectric phase transition indicating that the relaxation processes make contributions to the temperature evolution of the hard modes. This correlation and the anomalous behavior of the hard modes were observed for the first time;

* The distortion of the high-frequency A_{1g} mode, in the absence of a structural phase transition, is attributable to an increase in the crystal anharmonicity with decreasing temperature.

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[*] sergey.lushnikov@mail.ioffe.ru
[†] On leave from Ioffe Physical Technical Institute, 26 Politekhnicheskaya, 194021, St. Petersburg, Russia
[1] G.A. Smolenskii et al., Ferroelectrics and Related Materials, (Gordon and Breach, NY, 1984).
[2] L.E. Cross, Ferroelectrics **76**, 241 (1987).
[3] G. Burns and F. Dacol, Solid State Commun. **48**, 853 (1983); I.G. Siny and C. Boulesteix, Ferroelectrics **96**, 119 (1989); M.A. Akbas and P.K. Davies, J. Am. Ceram. Soc. **80**, 2933 (1997).
[4] J.-H. Ko, S. Kojima, S.G. Lushnikov, Appl. Phys. Lett. **82**, 4128 (2003).
[5] G.A. Smolensky, I.G. Siny, R.V. Pisarev, and E.G. Kuzminov, Ferroelectrics **12**, 135 (1976).
[6] I.G. Siny and T.A. Smirnova, Sov. Phys. Solid State **30**, 473 (1988); Ferroelectrics **90**, 191 (1989).
[7] S.N. Gvasaliya, B. Roessli, S.G. Lushnikov, Europhys. Lett. **63**, 303 (2003); S.N. Gvasaliya, S.G. Lushnikov, B. Roessli, Crystallography Reports **49**, 108 (2004).
[8] S.N.Gvasaliya, S.G.Lushnikov, I.L.Sashin, and T.A.Shaplygina, J. Appl. Phys. **94**, 1130 (2003).
[9] Yosuke Moriya, Hitoshi Kawaji, Takeo Tojo, and Tooru Atake, Phys. Rev. Lett. **90**, 205901 (2003).
[10] Z.G. Lu, C. Flicoteaux, G. Calvarin, Materials Research Bull. **31**, 445 (1996); S.N. Gvasaliya, B. Roessli, D. Sheptyakov *et.al.*, cond-mat/0406073 (2004); S.N. Gvasaliya, B. Roessli, D. Sheptyakov *et.al.*, Eur. Phys. J. B (2004) (in press).
[11] I.G.Siny, R.S.Katyar and A.S.Bhalla, J. Raman Spectrosc. **29**, 385 (1998).
[12] I.G. Siny, S.G. Lushnikov, R.S. Katiyar and V.H. Schmidt, Ferroelectrics **226**, 191 (1999).
[13] I.G. Siny, S.G. Lushnikov, R.S. Katiyar, and E.A. Rogacheva, Phys. Rev. B **56**, 7962 (1997).
[14] O. Svitelskiy, J. Toulouse, G. Yong, and Z.-G. Ye, Phys. Rev. B **68**, 104107 (2003).
[15] M.D. Fontana, E. Bouziane and G.E. Kugel, J. Phys.: Condens. Matter **2**, 8681 (1990).
[16] I.G. Siny, Ruiwu Tao, R.S. Katyar, Ruyan Guo, and A.S. Bhalla, J. Phys. Chem. Solids **59**, 181 (1998).
[17] E.K.H. Salje and U. Bismayer, Phase Transitions **63**, 1 (1997).
[18] V.L. Ginzburg, A.P. Levanyuk, A.A. Sobyanin in "Light scattering near phase transitions edited by H.Z. Cummins and A.P. Levanyuk, Modern problems in condensed matter science vol.5 (Amsterdam, North-Holland, 1983) p. 5.
[19] I.G. Siny, R.S. Katiyar and S.G. Lushnikov, in Proceedings of the XVth International Conference on Raman Spectroscopy, Edited by S.A. Asher (John Wiley & Sons, NY, 1996) p. 1002.